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[Name of Article] DRAWINGS 1

[Name of Article] ABSTRACT 1

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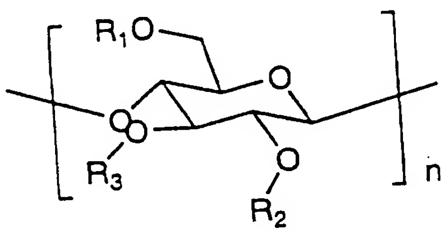
DESCRIPTION

LIQUID CRYSTAL MIXED-COMPOSITION AND RETARDATION FILM USING SAME

CLAIMS:

1. A liquid crystal mixed-composition comprising one or more cellulose derivatives and one or more liquid crystal compounds which can be oriented in a specific direction differing from that of said cellulose derivative as an essential component.

2. The liquid crystal mixed-composition according to claim 1, wherein the cellulose derivative has the following structure:



(1)

(wherein R_1, R_2 and R_3, which may be the same or different, respectively represent a hydrogen atom or a substituent, provided that R_1, R_2 and R_3 are not all hydrogen atoms and n denotes an integer of 10 or more);

3. The liquid crystal mixed-composition according to claim 2, wherein R_1, R_2 and R_3 are an acyloxyalkyl group and/or a carbamoyloxyalkyl group.

4. The liquid crystal mixed-composition according to any one of claims 1 to 3, wherein the mixing ratio of the cellulose derivative and the liquid crystal compound is that the former is 10 or more and 90 or less and the latter is 90 or more and 10 or less (ratio by weight).

5. A lyotropic liquid crystal mixed-composition comprising

the mixed-composition as claimed in any one of claims 1 to 4 and a reactive compound or an organic solvent, characterized by exhibiting a lyotropic liquid crystal state.

6. A retardation film which is produced by orienting the liquid crystal mixed- composition as claimed in any one of claims 1 to 5 on the rubbed substrate.

7. The retardation film according to claim 6, which is produced by being adjusted to establish the relation of Re450 ≤ Re550 ≤ Re650 between the retardation value (Re450) measured at a wavelength of 450 nm, the retardation value (Re550) measured at a wavelength of 550 nm and the retardation value (Re650) measured at a wavelength of 650 nm.

8. The retardation film according to any one of claim 6 or 7, which has a retardation of a quarter wavelength or a half wavelength.

9. A method of producing the retardation film according to any one of claims 6 to 8, characterized by controlling the relation of Re450, Re550 and Re650 of the retardation film by adjusting temperature for the orientation treatment after forming a layer of the liquid crystal composition as claimed in any one of claims 1 to 5 on a rubbed substrate.

10. A method of producing the retardation film according to any one of claims 6 to 8, characterized by controlling the relation of Re450, Re550 and Re650 of the retardation film by adjusting the orientation time for orientation treatment after forming a layer of the liquid crystal composition as claimed in any one of claims 1 to 5 on a rubbed substrate.

11. A circularly or elliptically polarizing film or a rotary polarizing film obtained by laminating the retardation film as claimed in any one of claims 6 to 8 and a polarizing film.

12. An image display device comprising the retardation film as claimed in any one of claims 6 to 8 or the circularly or elliptically polarizing film as claimed in claim 11.

DETAILED DESCRIPTION OF THE INVENTION

[0001]

TECHNICAL FIELD

The present invention relates to a liquid crystal composition used to prepare a retardation film useful for image display devices such as liquid crystal display devices and to a retardation film obtained from the liquid crystal composition.

[0002]

BACKGROUND ART

Retardation films obtained by uniaxially stretching plastic films such as polycarbonate, polyarylate and polyether sulfone are films having the function of changing the polarization axis of linearly polarized light (optical rotation) and the function of converting linearly polarized light into circularly polarized light or elliptically polarized light. This retardation film generally has so-called wavelength dispersion characteristics that a retardation differs depending on wavelength and the wavelength dispersion characteristics differ depending on the type of material to be used. Usually used retardation films each have the characteristics that the

retardation value in the wavelength side longer than 550 nm is smaller than the retardation value at a wavelength of 550 nm and the retardation value in the wavelength side shorter than 550 nm is larger than the retardation value at a wavelength of 550 nm. This tendency is more significant in the shorter wavelength side.

[0003]

This poses, for example, the problem that when a retardation film (so-called quarter wavelength plate) having a retardation which is to be 1/4 of the wavelength is used to produce an anti-reflection filter, a sufficient anti-reflection effect is obtained only in the wavelength range where the retardation is almost 1/4 the wavelength and circularly polarized light is converted into elliptically polarized light at other wavelengths with the result that only insufficient anti-reflection effect is obtained. Also, when a retardation film (so-called half-wave plate) having a retardation which is to be 1/2 of the wavelength is used to produce a rotary polarizer which is used for a liquid crystal projector and the like, only in the wavelength range where the retardation is almost 1/2 of the wavelength can rotate a linearly polarized light as linearly polarized light, and linearly polarized light is converted into elliptically polarized light at other wavelengths with the result that only an insufficient rotary polarizing effect is obtained.

[0004]

To deal with this problem, a method is proposed in which plural retardation films are laminated with their optical axis

being crossed with each other in the Patent Literature 1. This method, however, has the problem that it causes an increase in thickness due to the use of plural retardation films, such complexity of the production process in which plural retardation films are laminated with their optical axis being crossed with each other and a reduction in yield (these retardation films must be cut to cross these films with each other). In the meantime, a retardation film is proposed which can impart the same level of retardation to each wavelength in a wide visible range by using only one film in the Patent Literature 2.

[0005]

However, because the wavelength dispersion characteristics are determined by the material to be used in a retardation film, there is a limitation to such a material as described in the publication of Patent Literature 2 which can improve the wavelength dispersion characteristics by using only one film. Also, because such a material does not function as a retardation film unless it is made into a film and the film is further stretched uniaxially, such a complex step involving filming and stretching must be carried out. Further, as seen in circularly polarizing film, in the case where it is necessary to laminate the retardation films such that the polarization axis of a polarization film crosses at a specific angle with the slow axis of said retardation film, it is necessary to cut the film to laminate the cut film on another film even if the retardation film is one film, with the result that this causes a reduction in yield. In order to solve such a problem, a method

as described in the Patent Literature 3 in which using a liquid crystal compounds which can be oriented on a substrate which has been subjected to rubbing treatment and a composition obtained by mixing more than one of them, wherein said compound or composition is oriented in a specific direction to produce a retardation film has been known. A retardation film obtained by the method having such wavelength dispersion characteristics that the same level of retardation can be given to each wavelength in a wide visible range by the single film is described in the Patent Literature 4. However, it was not disclosed specific embodiments for orientation on a rubbed substrate.

[0006]

[Patent Literature 1] JP H5-100114 A (Pages 2 to 4)

[Patent Literature 2] JP 2000-137116 A (Pages 2 to 4)

[Patent Literature 3] JP 2000-98133 A (Pages 5 to 6 and 7)

[Patent Literature 4] Publication of PCT/JP02/04523 (Pages 23 to 24)

[Non-Patent Literature 1] Richard D. Gilbert, Cellulosic Polymers, Blends and Composites, Hanser Publishers, Pages 25 to 94

[0007]

PROBLEMS TO BE SOLVED BY THE INVENTION

The problem of the present invention is to provide materials to obtain a retardation film easily which can be oriented on a substrate which has been subjected to rubbing treatment and having such wavelength dispersion characteristics that the same level of retardation can be given to each wavelength

in a wide visible range by the single film and producing method thereof.

[0008]

MEANS OF SOLVING THE PROBLEMS

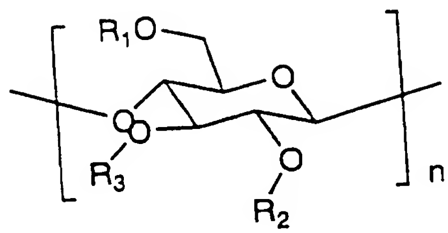
The inventors of the present invention have made earnest studies to solve the above problems and, as a result, found that by using a liquid crystal mixed-composition having specific composition, a layer of said composition is oriented on a rubbed substrate and then the orientation is fixed, whereby a retardation film can be obtained, in addition, not only the obtained retardation film has such wavelength dispersion characteristics that the same level of retardation can be given to each wavelength in a wide visible range by the single film, but also the wavelength dispersion characteristics can be fairly controlled by controlling the conditions under which the retardation film is manufactured, to complete the present invention.

[0009]

That is, the present invention relates to:

(1) A liquid crystal mixed-composition comprising one or more cellulose derivatives and one or more liquid crystal compounds which can be oriented in a specific direction differing from that of said cellulose derivative as an essential component,

(2) The liquid crystal mixed-composition according to claim 1, wherein the cellulose derivative has the following structure:



(1)

(wherein R_1, R_2 and R_3, which may be the same or different, respectively represent a hydrogen atom or a substituent, provided that R_1, R_2 and R_3 are not all hydrogen atoms and n denotes an integer of 10 or more),

(3) The liquid crystal mixed-composition according to claim 2, wherein R_1, R_2 and R_3 are an acyloxyalkyl group and/or a carbamoyloxyalkyl group,

(4) The liquid crystal mixed-composition according to any one of claims 1 to 3, wherein the mixing ratio of the cellulose derivative and the liquid crystal compound is that the former is 10 or more and 90 or less and the latter is 90 or more and 10 or less(ratio by weight),

(5) A lyotropic liquid crystal mixed-composition comprising the mixed-composition as claimed in any one of claims 1 to 4 and a reactive compound or an organic solvent, characterized by exhibiting a lyotropic liquid crystal state,

(6) The retardation film which is produced by orienting the liquid crystal mixed- composition as claimed in any one of claims 1 to 5 on the rubbed substrate,

(7) The retardation film according to claim 6, which is produced by being adjusted to establish the relation of $Re450 \leq Re550 \leq Re650$ between the retardation value (Re450) measured

at a wavelength of 450 nm, the retardation value (Re550) measured at a wavelength of 550 nm and the retardation value (Re650) measured at a wavelength of 650 nm,

(8) The retardation film according to any one of claim 6 or 7, which has a retardation of a quarter wavelength or a half wavelength,

(9) A method of producing the retardation film according to any one of claims 6 to 8, characterized by controlling the relation of Re450, Re550 and Re650 of the retardation film by adjusting temperature when the orientation treatment is carried out after forming a layer of the liquid crystal composition as claimed in any one of claims 1 to 5 on a rubbed substrate,

(10) A method of producing the retardation film according to any one of claims 6 to 8, characterized by controlling the relation of Re450, Re550 and Re650 of the retardation film by adjusting the time for orientation treatment when the orientation treatment is carried out after forming a layer of the liquid crystal composition as claimed in any one of claims 1 to 5 on a rubbed substrate,

(11) A circularly or elliptically polarizing film or a rotary polarizing film obtained by laminating the retardation film as claimed in any one of claims 6 to 8 and a polarizing film,

(12) An image display device comprising the retardation film as claimed in any one of claims 6 to 8 or the circularly or elliptically polarizing film as claimed in claim 11.

[0013]

EMBODIMENT OF THE INVENTION

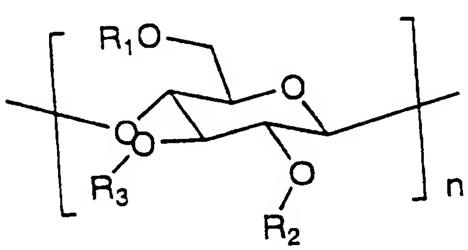
The present invention will be explained in detail.

The retardation film of the present invention is obtained by orientation a liquid crystal mixed-composition in a specific direction, the composition containing a cellulose derivative and a liquid crystal compound having a specific characteristics differing from said cellulose derivative. Many cellulose derivatives show liquid crystalline property; and, a cellulose derivative may be used for a liquid crystal mixed-composition of the present invention in both of the case where it is a thermotropic liquid crystal and the case where it is a lyotropic liquid crystal.

[0014] Examples of the cellulose derivative which may be used in the present invention include cellulose itself and cellulose in which hydroxy groups are chemically-modified represented by the following formula (1).

[0015]

[KA3]



(1)

[0016]

wherein R_1, R_2 and R_3 respectively represent a proton of a hydroxy group of cellulose or a substituent which has a structure may be the same or different. When a substituent is differing from each other, the abundance ratio of each substituent is optional.

Also, preferably n is an integer of 10 or more, more preferably 50 or more and further preferably 100 or more.

[0017]

Specific examples of R_1, R_2 and R_3 in the formula (1) include alkyl groups such as methyl group, ethyl group and propyl group, acyl groups such as an acetyl group and a propionyl group, nitrate ester groups, hydroxyalkyl groups such as hydroxypropyl group and hydroxyethyl group and further those obtained by acylating or carbamoylating the hydroxyalkyl groups. Among these compounds, those obtained by hydroxy-alkylating cellulose, followed by carbamoylating or acylating the hydroxy-alkylated cellulose are preferable, specifically, in which R_1, R_2 or R_3 is represented by the following formula; Y-CO-O-R- , or Z-NH-CO-O-R-. Here, R includes methylene group, ethylene group, trimethylene group, tetramethylene group, propylene group and the like, and Y includes (meta)acrylic group, methyl group, ethyl group, propyl group, isopropyl group, n-butyl group, isobutyl group, tert-butyl group, pentyl group, neopentyl group, hexyl group, cyclohexyl group, octyl group, nonyl group, decyl group, benzyl group, 1-naphthylmethyl group, trifluoromethyl group, aminomethyl group, 2-amino-ethyl group, 3-amino-n-propyl group, 4-amino-n-butyl group, or substituents obtained by converting these amino groups with amide or urethane, hydroxy substituted (C1-C4) alkyl groups or groups obtained by further substituting the hydroxy group with a (C1-C14) acyl group or (C1-C10) alkyl group, vinyl groups which may be substituted with a (C1-C3) alkyl group, cyanobiphenyloxy (C3-C10) alkyl groups, (C1-C10)

aliphatic groups, which have an unsaturated bond, such as acetylene group and cinnamoyl group, and acyl groups which has aromatic groups such as phenyl group, naphthyl group, anthracenyl group, fluorenyl group, biphenyl group and 4-trifluoromethylphenyl group, and Z includes (meta)acrylic group, methyl group, ethyl group, propyl group, isopropyl group, n-butyl group, isobutyl group, tert-butyl group, pentyl group, neopentyl group, hexyl group, cyclohexyl group, octyl group, nonyl group, decyl group, benzyl group, 1-naphthylmethyl group, trifluoromethyl group and the like, respectively.

As to these cellulose derivatives, one or more substituents are properly selected according to, for example, the temperature range where the target liquid crystal mixed-composition of the present invention exhibits liquid crystalline properties and the birefringence characteristics, wavelength dispersion characteristics, viscosity, orientating ability, processability and reactivity of the composition. Also, the degree of substitution of a hydroxyl group of the cellulose is appropriately selected according to, for example, the temperature range where the target liquid crystal mixed-composition of the present invention exhibits liquid crystalline properties and the birefringence characteristics, wavelength dispersion characteristics, viscosity, orientating ability, processability and reactivity of the composition.

[0018]

The liquid crystal mixed-composition of the present invention which can be oriented in a specific direction is

characterized by that a mixed-composition obtained from mixture of a cellulose derivative and a liquid crystal compound differing from said cellulose derivative possesses liquid crystalline properties deriving from the liquid crystal compound, or both of the liquid crystal compound and the cellulose derivative. The liquid crystal compound differing from the cellulose derivative using for a liquid crystal mixed-composition of the present invention preferably has liquid crystalline properties exhibiting thermotropic and a nematic phase, also, highly compatible with a cellulose derivative. Specific examples of such low-molecular liquid crystal include, for example, TL-202 (trade name, manufactured by Merck Company, mixture of low-molecular liquid crystals) and K-15 (trade name, manufactured by Merck Company, 4-cyano-4'-pentylbiphenyl), and acrylate type low-molecular liquid crystals such as 4-(4'-cyano-4-biphenylyloxy)-butylacrylate, liquid crystal compounds as described in the Patent Literature 3 having an acryloyl group and mixtures of these compounds and LPP F 301 CP (trade name, manufactured by Vantico Company, acrylate type low-molecular liquid crystal).

In the present invention, it is preferable to use an acrylate type low-molecular liquid crystal from the reason that the liquid crystal layer is easily fixed by irradiation with ultraviolet rays.

[0019]

Although the range where the mixed composition of the present invention exhibits liquid crystalline properties

differs depending on the type of cellulose derivative to be mixed and the type of liquid crystal compound differing from the cellulose derivative, the mixing ratio of the cellulose derivative to said liquid crystal compound is that the former is 10 or more and 90 or less and the latter is 90 or more and 10 or less, more preferably that the former is 15 or more and 70 or less and the latter is 85 or more and 30 or less. (both ratio by weight). Especially, the mixing ratio of the cellulose derivative to said liquid crystal compound is that the former is 20 or more and 50 or less and the latter is 80 or more and 50 or less (both ratio by weight) is particularly preferable not only because a composition layer of said mixing ratio can be oriented in the rubbing direction by forming a layer on a substrate rubbed under a proper condition, but also a retardation measured at a wavelength of 450nm (Re450), a retardation measured at a wavelength of 550nm (Re550) and a retardation measured at a wavelength of 650nm (Re650) of the retardation film of the present invention obtained by fixing or maintaining the orientation condition fulfill the relationship of Re450 ≤ Re550 ≤ Re650, in addition, the retardation film can provide the same level of retardation to each wavelength in a wide visible region.

[0020]

Mixing components other than the cellulose derivative and the liquid crystal compound differing from the cellulose derivative to the liquid crystal mixed-composition of the present invention may be added to the extent that the liquid crystalline properties of the composition are not impaired. These mixing

components are added to adjust the liquid crystalline properties, orientation ability, processability and component compatibility of the liquid crystal mixed- composition and to fix the orientation after the liquid crystal mixed-composition is oriented in a specific direction.

[0021]

In the present invention, a curable component may be contained as a mixing component in the liquid crystal mixed-composition of the present invention for the purpose of fixing the oriented state. In that casê, because the operating temperature limit of the liquid crystal compound is usually fixed, fixation by photopolymerization run by irradiation with ultraviolet rays which is relatively reduced in temperature change during polymerization is usually preferable and it is preferable to use a (meth)acrylate compound when such photopolymerization is run.

[0022]

The (meth)acrylate compounds include, for example, reaction products of trimethylolpropanetri(meth)acrylate, pentaerythritoltri(meth)acrylate, pentaerythritoltetra(meth)acrylate, ditrimethylolpropanetetra(meth)acrylate, dipentaerythritolpentaacrylate, dipentaerythritolhexaacrylate or pentaerythritoltri(meth)acrylate and 1,6-hexamethylenediisocyanate, reaction products of pentaerythritoltri(meth)acrylate and isophoronediisocyanate,

reaction products of tris(acryloxyethyl)isocyanurate, tris(methacryloxyethyl)isocyanurate or glyceroltriglycidyl ether and (meth)acrylic acids, reaction products of caprolactone-modified tris(acryloxyethyl)isocyanurate or trimethylolpropanetriglycidyl ether and (meth)acrylic acids, reaction products of triglyceroldi(meth)acrylate or propylene glycol diglycidyl ether and (meth)acrylic acids, reaction products of polypropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, pentaerythritol di(meth)acrylate or 1,6-hexanediol diglycidyl ether and (meth)acrylic acids, reaction products of 1,6-hexanedioldi(meth)acrylate, glycerol di(meth)acrylate or ethylene glycol diglycidyl ether and (meth)acrylic acids, reaction products of diethylene glycol diglycidyl ether and (meth)acrylic acids, reaction products of bis(acryloxyethyl)hydroxyethylisocyanurate, bis(methacryloxyethyl)hydroxyethylisocyanurate or bisphenol A diglycidyl ether and (meth)acrylic acids, reaction products of tetrahydrofurfuryl(meth)acrylate, caprolactone-modified tetrahydrofurfuryl(meth)acrylate, 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, polypropylene glycol (meth)acrylate, polyethylene glycol (meth)acrylate, phenoxyhydroxypropyl(meth)acrylate, acryloylmorpholine, methoxypolyethylene glycol (meth)acrylate, methoxytetraethylene glycol (meth)acrylate,

methoxytriethylene glycol (meth)acrylate, methoxyethylene glycol (meth)acrylate, methoxyethyl(meth)acrylate, glycidyl(meth)acrylate, glycerol(meth)acrylate, ethylcarbitol(meth)acrylate, 2-ethoxyethyl(meth)acrylate, N,N-dimethylaminoethyl(meth)acrylate, 2-cyanoethyl(meth)acrylate or butyl glycidyl ether and (meth)acrylic acids, butoxytriethylene glycol (meth)acrylate and butanediolmono(meth)acrylate. These compounds may be used either singly or by mixing plural compounds. A desired orientation state can be fixed by using such a reactive compound and polymerizing under appropriate conditions.

[0023]

When said composition can maintain the orientation condition without a reaction compound as a fixation agent, a compound as typically used as an organic solvent may be added. Such compound which is used to the extent that it does not impair the liquid crystalline properties of the mixed composition when it is blended, includes, for example, aliphatic hydrocarbons, aliphatic ketones, aliphatic amines and aliphatic alcohols such as hexane, heptane, acetone, cyclohexanone, cyclopentanone, triethylamine, 2-butanone, methanol, ethanol and isopropanol, further, aromatic hydrocarbons, aromatic amines and aromatic alcohols such as benzene, toluene, xylene, benzyl alcohol and benzylamine. These compounds may be formulated either singly or in combinations of two or more.

[0024]

The mixed composition obtained in this manner, for example,

is applied to the surface of a rubbed substrate, followed by removing the said composition by heating or the like if there is a compound used as an organic solvent, and the rest composition can be oriented in the rubbing direction and fixed as it is. The range where does not impair the liquid crystalline properties of the mixed composition, ratio by weight, the total of cellulose derivatives and low-molecular liquid crystal compounds is more than 3 to 1 of mixing components such as the above reactive compound or the organic solvent, more preferably more than 6, and further preferably more than about 9. As above, a composition which is maintaining crystalline properties-keeping state (referred to as lyotropic liquid crystal state) even in the case where a reactive compound or an organic solvent are added may be called a lyotropic liquid crystal mixed-composition.

[0025]

As the photopolymerization initiator, compounds used for usual ultraviolet-curable resins may be used. Specific examples of the compounds may be used include 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1 (Irgacure 907 manufactured by Ciba Specialty Chemicals Inc.), 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, manufactured by Ciba Specialty Chemicals Inc.), 4-(2-hydroxyethoxy)-phenyl(2-hydroxy-2-propyl) ketone (Irgacure 2959, manufactured by Ciba Specialty Chemicals Inc.), 1-(4-dodecylphenyl)-2-hydroxy-2-methylpropan-1-one (Darocure 953, manufactured by Merck Company), 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one

(Darocure 1116, manufactured by Merck Company), 2-hydroxy-2-methyl-1-phenylpropan-1-one (Irgacure 1173, manufactured by Ciba Specialty Chemicals Inc.), acetophenone type compounds such as diethoxyacetophenone, benzoin type compounds such as benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether and 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651, manufactured by Ciba Specialty Chemicals Inc.), benzophenone type compounds such as benzoylbenzoic acid, methyl benzoylbenzoate, 4-phenylbenzophenone, hydroxybenzophenone, 4-benzoyl-4'-methyldiphenyl sulfide and 3,3'-dimethyl-4-methoxybenzophenone (Kayacure MBP, manufactured by Nippon Kayaku Co., Ltd.), and thioxanthone type compounds such as thioxanthone, 2-chlorothioxanthone (Kayacure CTX, manufactured by Nippon Kayaku Co., Ltd.), 2-methylthioxanthone, 2,4-dimethylthioxanthone (Kayacure RTX), isopropylthioxanthone, 2,4-dichlorothioxanthone (Kayacure CTX, manufactured by Nippon Kayaku Co., Ltd.), 2,4-diethylthioxanthone (Kayacure DETX, manufactured by Nippon Kayaku Co., Ltd.) and 2,4-diisopropylthioxanthone (Kayacure DITX, manufactured by Nippon Kayaku Co., Ltd.). These photoinitiators may be used singly or may be used by mixing two or more in an each desired ratio.

[0026]

When benzophenone type compounds or thioxanthone type compounds are used, an adjuvant may be used to promote a photopolymerization reaction. Examples of such an adjuvant

include amine type compounds such as triethanolamine, methyldiethanolamine, triisopropanolamine, n-butylamine, n-methyldiethanolamine, diethylaminoethylmethacrylate, Michler's ketone, 4,4'-diethylaminophenone, ethyl 4-dimethylaminobenzoate, (n-butoxy)ethyl 4-dimethylaminobenzoate and isoamyl 4-dimethylaminobenzoate. The content of the photoinitiator is preferably about 0.5 parts by weight or more and about 10 parts by weight or less and more preferably about 2 parts by weight or more and about 8 parts by weight or less based on 100 parts by weight of the (meth)acrylate compound (including a liquid crystal polymer in the case where an acryloyl group is present in the polymer). Also, the content of the adjuvant is preferably about 0.5 equivalents to about 2 equivalents to the photoinitiator.

[0027]

The quantity of the radiation of ultraviolet rays is preferably about 100 to 1000 mJ/cm^2 though it differs depending on the type of the liquid crystal mixed-composition, the type and amount of the photoinitiator to be added and film thickness. A layer of the composition is cured in any of air atmosphere and inert gas (for example, nitrogen) atmosphere when it is irradiated with ultraviolet rays. However, if the film thickness is thinner, the layer is insufficiently cured due to an oxygenic hindrance. In such a case, it is preferable to irradiate the layer with ultraviolet rays in an inert gas atmosphere.

[0028]

Due to the liquid crystal mixed-composition of the present

invention is oriented on a rubbed substrate, by fixing or maintaining said orientation condition to produce the retardation film of the present invention. Specific method, for example, includes the liquid crystal mixed-composition of the present invention or the lyotropic liquid crystal mixed-composition diluted by adding a proper solvent (for example, acetate esters such as ethyl acetate, butyl acetate and methyl acetate; alcohols such as methanol, ethanol, propanol and isopropanol; along with methyl ethyl ketone, acetone, cyclopentanone, cyclohexane, toluene, xylene, anisole, hexane, heptane, and the like.) so as to apply it easily, then, is laminated on the rubbed surface of a substrate which has been subjected to rubbing treatment, for example, by application, after or on the process of removing the solvent by heating or the like, said composition should be under proper condition so as to keep liquid crystalline properties, it can be oriented, for example, in the same direction as the rubbing direction. Even if the oriented direction of the composition imperfectly accords to the rubbing direction, by figuring out the direction of orientation of the composition to the rubbing direction, orientation can be directed in an arbitrary direction.

Then, the state of orientation is fixed by the above method, (irradiation with ultraviolet rays in the presence of a photopolymerization initiator in the case of containing the reactive compound, and the like) to obtain the retardation film of the present invention. At this time, because the retardation of the obtained retardation film is determined by the product

of the birefringence of the oriented composition multiplied by the thickness of the composition layer, these factors may be properly adjusted according to the intended retardation of the retardation film.

[0029]

Examples of the substrate used in the case of carrying out rubbing treatment include a triacetylcellulose film and polyimide or polyvinyl alcohol thin films formed on the surface of a glass plate. Also, the rubbing treatment is carried out in the following method: so-called velvet rubbing cloth made of nylon, rayon or cotton is applied to a metal roll or plastic roll to manufacture a rubbing roll, which is then brought into contact with the surface of the substrate with rotating the roll while the rubbing roll or the substrate is moved in one direction. When the substrate is a lengthy plastic film, it is possible to carry out rubbing treatment continuously by rotating the rubbing roll put in a fixed state at a high speed while the substrate is carried with bringing the substrate into contact with the rubbing roll. The condition of the rubbing treatment differs depending on the type of substrate to be used, the percentage composition of the liquid crystal mixed-composition of the present invention, the diameter of the roll, the number of contact movements or the number of rotations and direction of rotation of the roll, the moving speed of the substrate or the roll and the pressure of the rubbing roll pressed to the substrate, and is therefore set according to the situation.

[0030]

The retardation film manufactured using the liquid crystal mixed-composition of the present invention preferably has the wavelength dispersion characteristics as shown by the following formula: Re450 ≤ Re550 ≤ Re650, between the retardation value (Re 450) measured at a wavelength of 450 nm, the retardation value (Re 550) measured at a wavelength of 550 nm and the retardation value (Re 650) measured at a wavelength of 650 nm. These wavelength dispersion characteristics can be controlled by the temperature and time when the composition is oriented. When the wavelength dispersion characteristics of the retardation film of the present invention by changing the temperature of the orientation treatment on the rubbed substrate are controlled, for example, on the rubbed substrate, with regard to the retardation film obtained by orientation the composition at 40°C when the mixing ratio of the cellulose derivative to the liquid crystal compound in the liquid crystal mixed-composition is that, for example, the former is 30 and the latter is 70, the retardation ratio at a wavelength of 450 nm (Re 450/Re 550) and the retardation ratio at a wavelength of 650 nm (Re 650/Re 550) are 0.75 and 1.06 respectively. When the orientation temperature is changed to 55°C, (Re 450/Re 550) and (Re 650/Re 550) can be 0.76 and 1.07 respectively.

[0031]

Also, when the wavelength dispersion characteristics of the retardation film of the present invention by changing the time of the orientation treatment of the liquid crystal mixed-composition on the rubbed substrate are controlled, with

regard to the retardation film obtained by orientation at 40°C for 30 minutes when the mixing ratio of the cellulose derivative to the liquid crystal compound in the liquid crystal mixed-composition is adjusted, for example, the former is 20 and the latter is 80, the retardation ratio at a wavelength of 450 nm (Re 450/Re 550) and the retardation ratio at a wavelength of 650 nm (Re 650/Re 550) are 0.84 and 1.01 respectively. When the orientation time is changed for 22 hours, (Re 450/Re 550) and (Re 650/Re 550) can be 0.69 and 1.07 respectively.

[0032]

The retardation film obtained in this manner according to the present invention and the used polarizing film are laminated such that the slow axis of the retardation film of the present invention forms a predetermined angle with the absorption axis of the polarizing film, whereby the elliptically polarizing film can be obtained. Also, the retardation value of the retardation film of the present invention at a wavelength of 550 nm is made to be about 137 nm and the retardation film obtained in this manner according to the present invention and the polarizing film are laminated such that the slow axis of the retardation film forms an angle of 45° with the absorption axis of the polarizing film, whereby the circularly polarizing film of the present invention can be obtained. Moreover, the retardation value of the retardation film of the present invention at a wavelength of 550 nm is made to be about 275 nm and the polarizing film and the retardation film are laminated such that the absorption axis of the polarizing film forms an

angle of 45° with the slow axis of the retardation film, whereby the rotary polarizing film of the present invention can be obtained. The circularly polarizing film obtained in this manner according to the present invention is used in, for example, a reflection type or a reflection semi-transmittable type liquid crystal display device or the rotary polarizing film of the present invention is used in a liquid crystal projector, and thus an image display device according to the present invention can be obtained. If, particularly, the wavelength dispersion characteristics of the circularly polarizing plate are such that the retardation is almost 1/4 of each wavelength in the visible region, linearly polarized light can be converted into circularly polarized light in a wide wavelength range. Therefore, an image display device having a more excellent reflection preventive effect and contrast-improving effect than a circularly polarized plate using usual polycarbonate can be obtained.

[0033]

The rotary polarizing film of the present invention can rotate the polarization axis of linearly polarized light without converting the linearly polarized light into elliptically polarized light in a wide wavelength range if the wavelength dispersion characteristics of the retardation film are such that the retardation is almost 1/2 of each wavelength in the visible region. Therefore, if the rotary polarizing film is used in a liquid crystal projector, light-utilization efficiency can be improved and a deterioration of a polarizing film caused by absorption of light can be prevented. Since the retardation film

of the present invention enables the liquid crystal mixed-composition to be oriented in a rubbing direction by rubbing treatment and it is therefore possible to change the direction of the slow axis by changing the rubbing direction. This ensures that a retardation film in which the slow axis inclines at 45° with the longitudinal direction can be produced, for example, by using a roll-like lengthy high-molecular film, rubbing the film in a direction at 45° with the longitudinal direction, then forming a layer of the liquid crystal mixed- composition of the present invention and orientation the composition in the rubbing direction. This retardation film and a polarizing film (polarizing films obtained by usual uniaxial orientation have a roll-like form and its absorption axis extending in the longitudinal direction) are laminated by a roll-to-roll method to thereby obtain the aforementioned circularly polarizing film and rotary polarizing film. This method makes it possible to make an improvement in yield more significantly than in the case of cutting one of a uniaxially stretched polarizing film and a retardation film to laminate.

[0034]

EXAMPLES

The present invention will be explained in more detail by way of examples.

[0035]

EXAMPLE 1

900 ml of acetone was added in a reaction container charged with 30.0 g of hydroxypropyl cellulose HPC (manufactured by

Aldrich Company, molecular weight: 100,000) and the mixture was refluxed under heating in an 80°C bath. After it was confirmed that the mixture was completely dissolved, the temperature of the reaction solution was dropped to room temperature. Then, 76.1 ml of triethylamine and then, 62.2 ml of pivaloyl chloride were added to the reaction solution. After the mixture was stirred at room temperature for 5 minutes, it was stirred for 4 and half hours in a 75°C bath. An enameled container was charged with 18 L of water, followed by stirring, to which was then added the reaction solution and the resulting mixture was allowed to stand for while. The precipitates produced by this reprecipitation operation were washed with flowing water several times and then dissolved under heating in 1.8 L of acetone. After a reprecipitation operation was performed using 18 L of water and the crystals were washed with flowing water, 31.0 g of a pivaloyl compound of hydroxypropyl cellulose ($((CH_3)_3CO-)$HPC to be intended was obtained. The degree of substitution of a pivaloyl group based on the mol number of hydroxyl groups of the reaction raw material HPC was about 70%. This compound was observed to have a texture peculiar to cellulose having liquid crystalline properties by the shearing of a cast film.

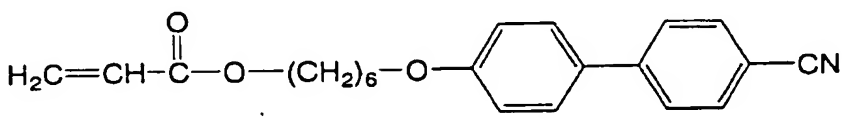
[0036]

Next, 9 of methyl ethyl ketone was added to 1 of the pivaloyl compound of hydroxypropyl cellulose and swelled and dissolved to obtain a solution having a solid content of 10% by weight. To this solution were added a liquid crystal compound which was a mixture of ultraviolet-curable liquid crystal compounds as

described in the Patent Literature 3 (hereinafter referred to a compound as described in the Patent Literature 3), specifically, 25 parts by weight of a compound represented by the following formula:

[0037]

[KA4]

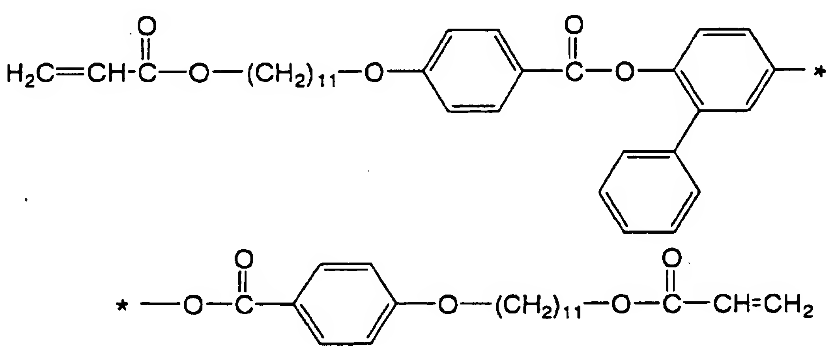


[0038]

and 75 parts by weight of a compound represented by the following formula:

[0039]

[KA5]



[0040]

(in the formula, * shows that the groups on both sides thereof are bonded with each other.)

a reactive compound which was 1,6-hexanedioldiacrylate (Kayarad HDDA, manufactured by Nippon Kayaku Co., Ltd.) and a photoinitiator which was 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, manufactured by Ciba Specialty Chemicals, Inc.)

in the following ratio by weight: cellulose derivative : liquid crystal compound : reactive compound : photoinitiator : methyl ethyl ketone = 20 : 80 : 2 : 4 : 180, to obtain a liquid crystal mixed-composition according to the present invention.

Then, an aqueous 1% solution of polyvinyl alcohol KM-11 (manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.) was applied to a glass plate and dried by hot air. Then, the dried layer was rubbed 20 times by a roll around which a rubbing cloth YA-20R was wound. The solution of the liquid crystal mixed-composition which was prepared previously was applied to the rubbed surface by using a bar coater RDS-04, dried at 100°C for one minute and kept on a 100°C hot plate for 30 seconds. After that, the coated surface was irradiated with light from a high-pressure mercury lamp (80 W/cm) to fix the coated surface to obtain a retardation film according to the present invention. The retardation of the obtained retardation film was 86 nm. Then, the retardation value of this retardation film at each wavelength was measured using an automatic birefringence meter (KOBRA-21ADH, manufactured by Ohji Keisoku) to find the ratio (wavelength dispersion characteristics) of the retardation value at each wavelength to the retardation value at a wavelength of 550 nm. The results are shown in Fig. 1.

[0041]

EXAMPLE 2

100 ml of acetone was added in a reaction container charged with 5.0 g of hydroxypropyl cellulose HPC (manufactured by Aldrich Company, molecular weight: 100,000) and the mixture was

refluxed under heating in an 80°C bath. After it was confirmed that the mixture was completely dissolved, the temperature of the reaction solution was dropped to room temperature. Then, 12.5 ml of acryloyl chloride was added to the reaction solution, which was then stirred at room temperature for one hour and under reflux for 1.5 hours. Thereafter, 5.0 ml of propionyl chloride was added to the reaction mixture, which was then stirred for 30 minutes and also stirred under reflux for 1.5 hours. The reaction content was poured into 3 L of water to reprecipitate and the precipitated crystals were washed with water. Then, the crystals were dissolved under heating in 100 ml of acetone to repeat a reprecipitation operation three times by using 3 L of water. After water was thoroughly drained off, the precipitates were dried under vacuum in a light-shading condition to obtain 5.0 g of an acryloyl-propionyl compound of hydroxypropyl cellulose (CH_2CHCO-) (C_2H_5CO-)HPC. The degree of substitution of an acryloyl group based on the mol number of hydroxyl groups of the reaction raw material HPC was about 30% and the degree of substitution of a propionyl group based on the mol number of hydroxyl groups of the reaction raw material HPC was about 30%. This compound had selective reflection characteristics specific to a cholesteric liquid crystal and was observed to have a texture peculiar to a cholesteric liquid crystal cellulose when a cast film is sheared. Next, 9 of methyl ethyl ketone was added to 1 of the acryloyl-propionyl compound of hydroxypropyl cellulose and swelled and dissolved to obtain a solution having a solid content of 10% by weight. To this solution were added

the compound as described in the Patent Literature 3 used in Example 1 as a compound doubling as a liquid crystal compound and a reactive compound and 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, manufactured by Ciba Specialty Chemicals) as a photoinitiator in the following ratio: cellulose derivative : liquid crystal compound : photoinitiator : methyl ethyl ketone = 20 : 80 : 4 : 180, to obtain a liquid crystal mixed-composition according to the present invention.

[0042]

Then, an aqueous 1% solution of polyvinyl alcohol KM-11 was applied to a glass plate and dried by hot air. Then, the dried layer was rubbed 50 times by a roll around which a rubbing cloth YA-20R was wound. The solution of the liquid crystal mixed-composition which was prepared previously was applied to the rubbed surface by using a bar coater RDS-06, dried at 100°C for one minute and kept on a 100°C hot plate for 30 seconds. After that, the coated surface was irradiated with light from a high-pressure mercury lamp (80 W/cm) to fix the coated surface to obtain a retardation film according to the present invention. The retardation value of the obtained retardation film was 67 nm. Then, the wavelength dispersion characteristics of this film were found in the same manner as in Example 1. The results are shown in Fig. 1.

[0043]

EXAMPLE 3

7.1 parts by weight of the pivaloyl compound of hydroxylpropyl cellulose used in Example 1, 28.6 parts by weight

of the mixture of the compound as described in the Patent Literature 3 as a liquid crystal compound used in Example 1 and 64.3 parts by weight of methyl ethyl ketone were used to prepare a solution of a liquid crystal mixed-composition according to the present invention such that the concentration of a cellulose derivative after drying was 20% by weight.

Then, an aqueous 1% solution of polyvinyl alcohol KM-11 was applied to a glass plate and dried by hot air. Then, the dried layer was rubbed 50 times by a rubbing cloth YA-20R. The solution of the liquid compound composition which was prepared previously was applied to the rubbed surface by using a bar coater RDS-06, dried at 100°C for one minute and kept on a 100°C hot plate for 30 seconds and at room temperature for 72 hours, to obtain a retardation film according to the present invention. The retardation value of the obtained retardation film was 97 nm. Then, the wavelength dispersion characteristics of this film were found in the same manner as in Example 1. The results are shown in Fig. 1.

[0044]

EXAMPLE 4

8.1 parts by weight of the pivaloyl compound of hydroxylpropyl cellulose used in Example 1, 18.9 parts by weight of the compound as described in the Patent Literature 3 as a liquid crystal compound used in Example 1 and 73 parts by weight of methyl ethyl ketone were used to prepare a solution of a liquid crystal mixed-composition according to the present invention such that the concentration of a cellulose derivative after

drying was 30% by weight. The retardation value of the obtained retardation film which was measured in the same manner as in Example 1 was 116 nm. Then, the wavelength dispersion characteristics of this film were found in the same manner as in Example 1. The results are shown in Fig. 1.

[0045]

EXAMPLE 5

8.7 parts by weight of the pivaloyl compound of hydroxylpropyl cellulose used in Example 1, 13.0 parts by weight of the compound as described in the Patent Literature 3 used in Example 1 as a liquid crystal compound used in Example 1 and 78.3 parts by weight of methyl ethyl ketone were used to prepare a solution of a liquid crystal mixed-composition according to the present invention such that the concentration of a cellulose derivative after drying was 40% by weight. The retardation value of the retardation film which was measured in the same manner as in Example 1 was 82 nm. Then, the wavelength dispersion characteristics of this film were found in the same manner as in Example 1. The results are shown in Fig. 1.

[0046]

EXAMPLE 6

The condition under which the retardation film of the present invention was kept after dried in the production of the film in Example 3 was changed to 40°C and 22 hours. The retardation value of the obtained retardation film was 121 nm. Then, the wavelength dispersion characteristics of this film were found in the same manner as in Example 1. The results are shown in

Fig. 2.

[0047]

EXAMPLE 7

The condition under which the retardation film of the present invention was kept after dried in the production of the film in Example 3 was changed to 55°C and 28 hours. The retardation value of the obtained retardation film was 37 nm. Then, the wavelength dispersion characteristics of this film were found in the same manner as in Example 1. The results are shown in Fig. 2.

[0048]

EXAMPLE 8

The condition under which the retardation film of the present invention was kept after dried in the production of the film in Example 3 was changed to 40°C and 30 minutes. The retardation value of the obtained retardation film was 137 nm. Then, the wavelength dispersion characteristics of this film were found in the same manner as in Example 1. The results are shown in Fig. 3.

[0049]

EXAMPLE 9

The condition under which the retardation film of the present invention was kept after dried in the production of the film in Example 3 was changed to 40°C and 6 hours. The retardation value of the obtained retardation film was 101 nm. Then, the wavelength dispersion characteristics of this film were found in the same manner as in Example 1. The results are shown in

Fig. 3.

[0050]

COMPARATIVE EXAMPLE

The wavelength dispersion characteristics of a polycarbonate retardation film (retardation: 140 nm) were evaluated in the same manner as in Example 1. The results are shown in Fig. 1.

[0051]

From the results of comparison of the wavelength dispersion characteristics of each retardation film obtained in Example 1 to 5 and Comparative Example, it is found that the retardation film of the present invention has the characteristics that the retardation value in the wavelength side longer than 550 nm is larger than the retardation value at a wavelength of 550 nm and the retardation value in the wavelength side shorter than 550 nm is smaller than the retardation value at a wavelength of 550 nm and also found that the retardation film of the present invention provides almost equal retardation to each wavelength. Also, from the results of comparison between Examples 6 and 7, it is found that the wavelength dispersion characteristics can be changed by changing the temperature at which the retardation film is kept (orientation temperature) in the production of the retardation film of the present invention. Also, from the results of comparison between Examples 8 and 9, it is found that the wavelength dispersion characteristics can be changed by changing the time during which the retardation film is kept in the production of the retardation film of the present invention.

[0052]

EFFECT OF THE INVENTION

The present invention is a liquid crystal mixed-composition comprising a cellulose derivative and a liquid crystal compound, and by orientation it in a specific direction, a retardation film can be produced. If this retardation film is used, retardation films having various wavelength dispersion characteristics can be produced without laminating plural retardation films. The retardation film obtained in this manner may be used in combination with a polarizing film as a circularly or elliptically polarizing film or rotary polarizing film in applications of various image display devices, whereby, for example, an excellent reflection preventive effect, contrast-improving effect and birefringence compensation effect can be obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

[Fig. 1] is a graph showing the wavelength dispersion characteristics of each retardation film obtained in Examples 1 to 5 and Comparative Example.

[Fig. 2] is a graph showing the wavelength dispersion characteristics of each retardation film obtained in Examples 6 and 7.

[Fig. 3] is a graph showing the wavelength dispersion characteristics of each retardation film obtained in Examples 8 and 9.

Fig. 1

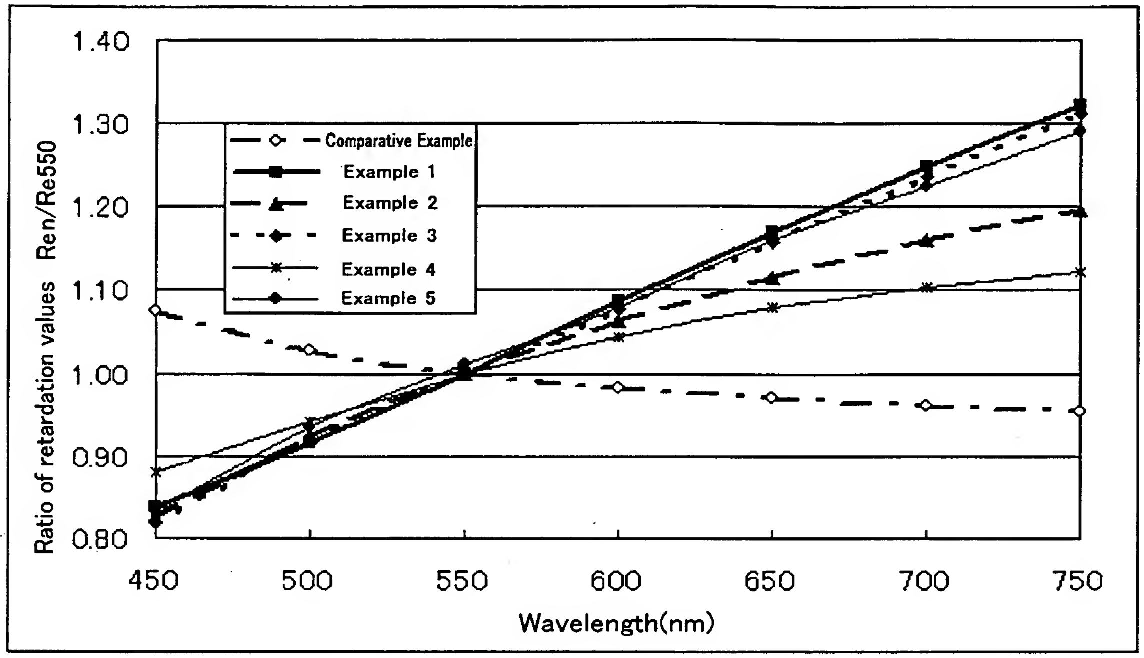
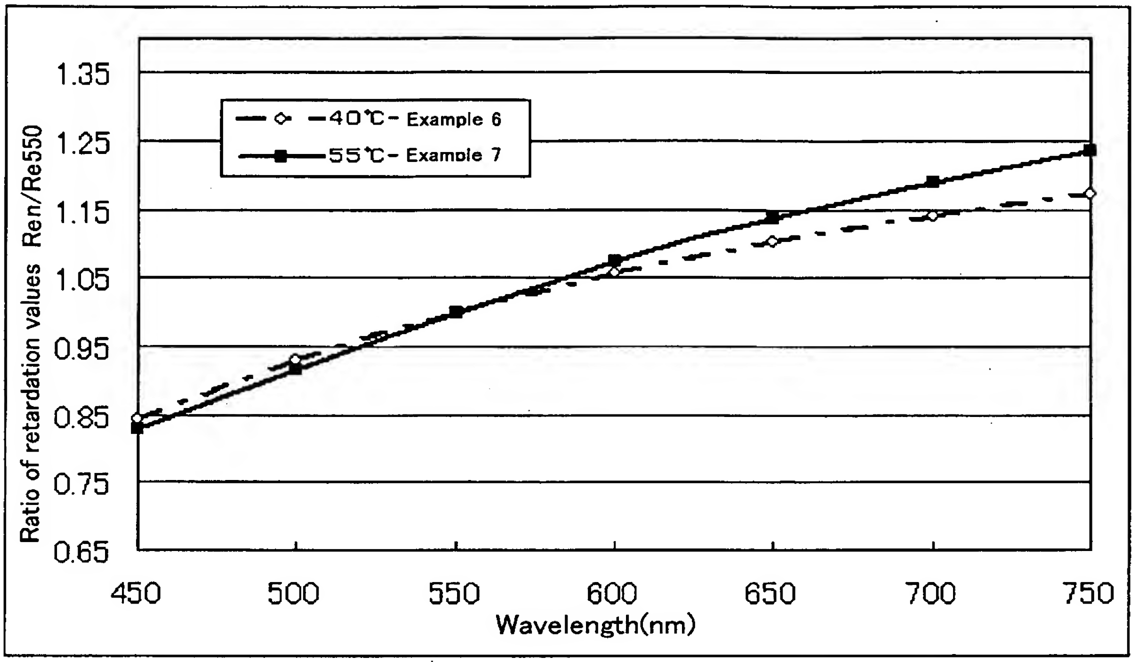
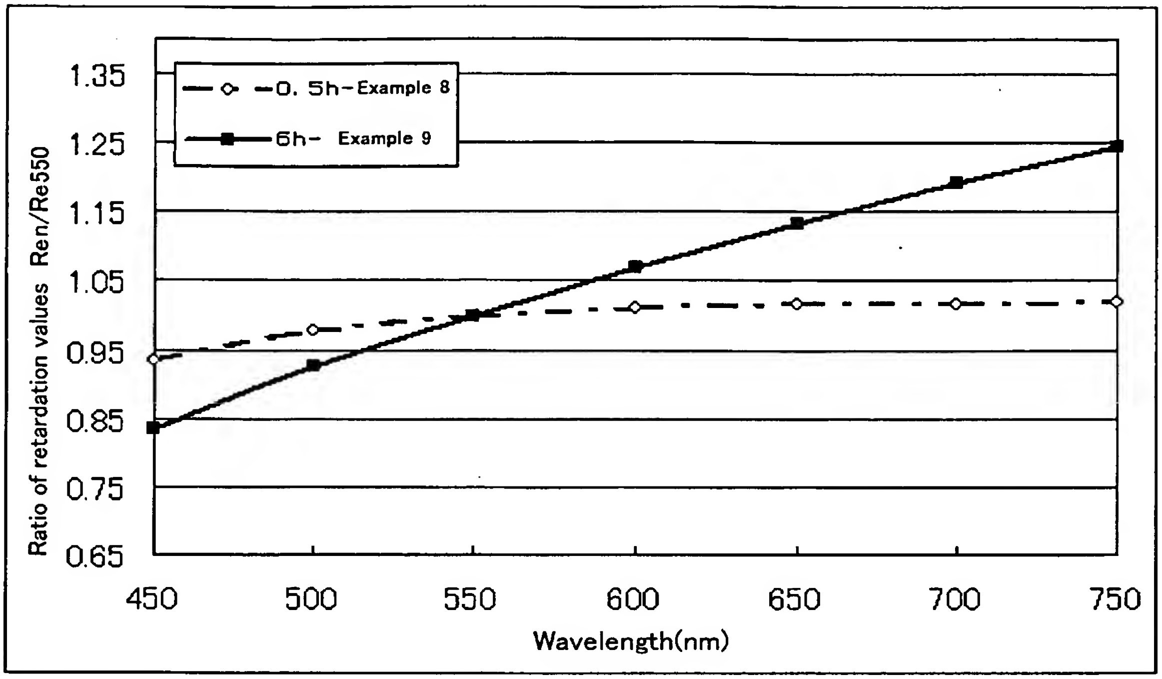

1.40
1.30
1.20
1.10
1.00
0.90
0.80
Ratio of retardation values Ren/Re550
Comparative Example
Example 1
Example 2
Example 3
Example 4
Example 5
450
500
550
600
650
700
750
Wavelength(nm)

Fig. 2



1.35
1.25
1.15
1.05
0.95
0.85
0.75
0.65
Ratio of retardation values Ren/Re550
40℃- Example 6
55℃- Example 7
450
500
550
600
650
700
750
Wavelength(nm)

Fig. 3



0. 5h-Example 8
6h- Example 9
Ratio of retardation values Ren/Re550
1.35
1.25
1.15
1.05
0.95
0.85
0.75
0.65
450
500
550
600
650
700
750
Wavelength(nm)

ABSTRACT

PROBLEM

To provide a retardation film having various wavelength dispersion characteristics without laminating multiple retardation films.

SOLVING MEANS

A liquid crystal mixed-composition comprising a cellulose derivative and a liquid crystal compound, and a retardation film obtained by orientation it in a specific direction.

REPRESENTATIVE DRAWING

None

CERTIFICATE OF VERIFICATION

I, Etsuko MIYAMOTO, a national of Japan, c/o SAEKI & PARTNERS of 4th Floor, Aminosan Kaikan Bldg., 15-8, Nihonbashi 3-chome, Chuo-ku, Tokyo, 103-0027 JAPAN do hereby solemnly and sincerely declare:

1) THAT I am well acquainted with the Japanese language and the English language, and
2) THAT the attached is a true, accurate and faithful translation into the English language made by me of Japanese Patent Application No. 2002-325656 filed to the Japanese Patent Office November 8, 2002.

Signed this 7th day of April, 2008.

Etsuko Miyamoto

Etsuko MIYAMOTO